Modeling Hydrate Formation in Media with Broad Pore Size Distributions

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We show how the modification by Henry et al. of the earlier van der Waals–Plateeuw thermodynamic model can be used to interpret data for hydrates in small pores even when there is a broad distribution of pore sizes. Pore size distribution effects explain the previously reported discrepancy between calculated and measured equilibrium pressures for nominal 7.5 nm radius pores. On the basis of the model, pore volume distributions are reconstructed for the silica gel samples in which the hydrates were formed and compared with distributions constructed from desorption isotherms. The excellent agreement between the calculations and experimental data supports the interpretation of how the pore size distribution present in the silica gel samples affects the observed equilibrium pressures.

Introduction

Gas hydrates are crystalline structures, belonging to a group of solids known as clathrates, which involve a lattice made up of hydrogen-bonded water molecules containing cavities occupied by guest gas molecules. Gas hydrates form under low temperature–high pressure conditions, both above and below the freezing point of water. Under proper conditions the lattice is stabilized by van der Waals forces through the occupation of specific cavities within the lattice by certain types of guest molecules. The type of guest molecule(s) present determines which of three known crystal structures the lattice assumes.[1,2]

Interest in natural gas hydrates is in part due to their presence under two different types of conditions. The first is related to their formation in manmade environments such as pipelines. When hydrates form, they tend to do so in aggregates, with a high potential of blocking pipelines if allowed to form unchecked. The second set of conditions are those found in nature, where hydrates form in permafrost regions and beneath deep oceans, where they are commonly found in sediment pores, acting as a cement holding the sediment together. While many experimental data are available concerning hydrate formation under bulk conditions (similar to those found in pipelines), only a very few studies have addressed hydrate formation in porous media. Handa and Stupin[3] reported equilibrium pressure–temperature data for both methane and propane hydrates in 7 nm nominal radius silica gel pores. Henry et al.[4] and Clarke et al.[5] reported calculations, based on earlier statistical thermodynamic models, aimed at ex-

plaining the observed differences between the equilibrium pressures observed in the bulk and in these pores. Both calculations resulted in large discrepancies between the observed and predicted pressure values. Experimental data for propane hydrate formation in pores with 2, 3, 5, and 7.5 nm radii silica gel pores have recently been presented.[6] In this work we address the discrepancy between the observed and predicted equilibrium pressures for hydrate formation in silica gel pores reported in these works by accounting for the effects of the pore size distribution. While Uchida et al.[7] examined methane hydrate formation in various sized Vycor glass pores, comparison with these data is not possible since their experimental pressure–temperature points were only reported in graphical form. [While Uchida et al.[7] tabulated inferred "final" dissociation pressure–temperature points for each experiment, they did not tabulate the very many experimental data used to obtain these inferred points.]

The Thermodynamic Model

The equilibrium conditions for the formation of hydrates in pure water and the methods to calculate them are well established. The calculations are based on the assumption that there is equilibrium between the water in the hydrate phase and that in the coexisting pure water phase such that the chemical potentials are equal

$$\mu_H = \mu_\alpha \tag{1}$$

where μ_H is the chemical potential of the water in the hydrate phase and μ_α is that in the pure water. The statistical thermodynamic models used in the calculation of the chemical potential of the water in the hydrate phase are based on the van der Waals and Plateeuw[8] adsorption

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(2) Sloan, E. D. *Clathrate Hydrates of Natural Gases*, 2nd ed.; Marcel Dekker: New York, 1997.
(3) Handa, Y. P.; Stupin, D. *J. Phys. Chem.* **1992**, *96*, 8599.
(4) Henry, P.; Thomas, M.; Clennell, M. B. *J. Geophys. Res.* **1999**, *104*, 23005.
(5) Clarke, M. A.; Pooladi-Darvish, M.; Bishnoi, P. R. *Ind. Eng. Chem. Res.* **1999**, *38*, 2485.
(6) Seshadri, K.; Wilder, J. W.; Smith, D. H. *J. Phys. Chem. B* **2001**, *105*, 2627.
(7) Uchida, T.; Ebinuma, T.; Ishizaki, T. *J. Phys. Chem. B* **1999**, *103*, 3659.
(8) van der Waals, J. H.; Plateeuw, J. C. *Adv. Chem. Phys.* **1959**, *2*, 1.

model, which for systems involving a single hydrate former can be written in the form

$$\Delta\mu_H = \mu_\beta - \mu_H = -RT\sum_i \eta_i \ln(1 - Y_i) \quad (2)$$

In eq 2 μ_β is the chemical potential of the water in a hypothetical empty lattice, η_i is the number of cavities of type i in the hydrate lattice, and Y_i denotes the probability of a cavity of type i being occupied by the guest molecule and is given in terms of the fugacity of the hydrate guest in the gaseous state (f_i) and the Langmuir adsorption constant (C_i) by

$$Y_i = \frac{C_i f_i}{1 + C_i f_i} \quad (3)$$

In the present model the temperature dependence of the Langmuir constants is accounted for by using the form presented by Munck et al.,[9] $C_i = (A_i/T) \exp(B_i/T)$, where A_i and B_i are experimentally fit parameters and are dependent on which guest molecule is present. Other researchers[2,10,11] have used Kihara potential functions to model these constants. Since this approach also involves parameters that are adjusted to fit the model predictions to experimental data, we use the above formulation due to its ease of use.

Holder et al.[10] compute the chemical potential difference between the water in the empty lattice and the pure state using

$$\frac{\Delta\mu_W}{RT_f} = \frac{\Delta\mu_W^0}{RT_0} - \int_{T_0}^{T_f}\frac{\Delta H_w}{RT^2} dT + \int_0^{P_f}\frac{\Delta V_w}{RT_f} dP - \ln(\gamma_w X_w) \quad (4)$$

where T_f and P_f are the temperature and pressure at which the hydrate forms, T_0 is the temperature of the standard reference state ($T = 273.15$ K, $P = 0$), and $\Delta\mu_W^0$ is the chemical potential difference for the reference state. The second term on the right-hand side of eq 4 accounts for the temperature dependence (at zero pressure) by assuming $\Delta H_W = \Delta H_W^0 + \int_{T_0}^T \Delta C_p(T') dT'$, where ΔH_W^0 is a reference enthalpy difference between the empty hydrate lattice and the pure water phase at the reference temperature. The temperature dependence of the heat capacity difference between these two states is modeled as[11] $\Delta C_p(T') = \Delta C_p^0 + b(T - T_0)$, where ΔC_p^0 is the reference heat capacity difference and b is a constant. The third term on the right-hand side of (4) corrects for the pressure dependence and involves ΔV_W, the volume difference between the empty hydrate and pure solid or liquid water (at T_0), and is assumed constant (but different for the two phases). The last term in (4) is a correction to the chemical potential of pure water due to the solubility of the guest molecule.

Combining (1), (2), and (4) leads to a single equation involving T_f and P_f, the temperature and pressure under which the hydrate forms

(9) Munck, J.; Skjold-Jörgensen, S.; Rasmussen, P. *Chem. Eng. Sci.* **1988**, *43*, 2661.
(10) Holder, G. D.; Corbin, G.; Papadapoulos, K. D. *Ind. Eng. Chem. Fundam.* **1980**, *19*, 282.
(11) Holder, G. D.; Zetts, S. P.; Prodhan, N. *Rev. Chem. Eng.* **1988**, *5*, 1.

$$\frac{\Delta\mu_W^0}{RT_0} - \int_{T_0}^{T_f}\frac{\Delta H_w}{RT^2} dT + \int_0^{P_f}\frac{\Delta V_w}{RT_f} dP - \ln(\gamma_w X_w) +$$

$$\sum_i \eta_i \ln(1 - Y_i) = 0 \quad (5)$$

If used in concert with an equation of state for the guest (to calculate the fugacity needed in (3)) and a solubility model (to calculate X_w), this equation can be solved using an iterative procedure for the pressure P_f at a chosen temperature T_f.

Recent works[4,5] have made modifications to this procedure to allow for the consideration of hydrate formation in small pores where the effects of the curvature of the interface between water and hydrate (and/or water and gas) are appreciable due to the resulting capillary pressure. As suggested by Henry et al.,[4] we assume that the experimental conditions imply that the pore hydrate and not the pore water is in equilibrium with the gas. Therefore, we consider the effect of capillary pressure on the chemical potential difference between the empty hydrate lattice and the pure water phase to be given by

$$(\Delta\mu_W)_{pore} = (\Delta\mu_W)_{bulk} + V_L\frac{2\cos(\theta)\sigma_{hw}}{r} \quad (6)$$

where V_L is the molar volume of water in the pure water state, θ is the wetting angle between the pure water phase and the hydrate, σ_{hw} is the surface tension between the water and hydrate phases, and r is the radius of the pore. [Note that while the equations used by Clarke et al.[5] are similar in appearance to those presented here, they involve inherently different assumptions about the hydrate interface.] With this addition, eq 4 becomes

$$\frac{\Delta\mu_W^0}{RT_0} - \int_{T_0}^{T_f}\frac{\Delta H_w}{RT^2} dT + \int_0^{P_f}\frac{\Delta V_w}{RT_f} dP - \ln(\gamma_w X_w) +$$

$$\sum_i \eta_i \ln(1 - Y_i) + V_L\frac{2\cos(\theta)\sigma_{hw}}{rRT_f} = 0 \quad (7)$$

In the application of eq 7 it is essential that care be taken to account for the effect of restricted geometry on the freezing point of water. For example, water in a spherical pore of radius r has a melting point given by[12]

$$T_m^{pore} = T_m^{bulk}\left[1 - \frac{2\sigma_{iw}}{\rho_w\Delta H_{fw}r_b}\right] \quad (8)$$

where T_m^{bulk} is the bulk melting temperature (273.15 K), σ_{iw} is the surface tension (0.0267 J/m²) between water and ice,[4] ρ_w is the specific density of water (1000 kg/m³), ΔH_{fw} is the specific enthalpy of fusion of water (333 kJ/kg), and r_b is the effective pore radius (which may be different from the nominal pore radius).[12] As a result, the quadruple point temperature, T_{Q1} (the temperature at which liquid water, ice, gas, and hydrate are all in equilibrium), will decrease from its bulk value as the pore size decreases. Therefore, the integral in the second term of eq 7 must be treated differently from when $T_{Q1} = T_0$, since only in the region $T < T_{Q1}$ is ice present. Since there are different functions for ΔH_W in the liquid and solid regions, the integral must be taken using the correct forms. The second term in eq 7 is thus given by

(12) Jallut, C.; Lenoir, J.; Bardot, C.; Eyrand, C. *J. Membr. Sci.* **1992**, *68*, 271.

$$\int_{T_0}^{T_f} \frac{\Delta H_W}{RT^2} \, dT =$$

$$\begin{cases} \int_{T_0}^{T_f} \frac{\Delta H_W^{liq}}{RT^2} \, dT, & T_f > T_{Q1} \\ \int_{T_0}^{T_{Q1}} \frac{\Delta H_W^{liq}}{RT^2} \, dT + \int_{T_{Q1}}^{T_f} \frac{\Delta H_W^{sol}}{RT^2} \, dT, & T_f < T_{Q1} \end{cases} \tag{9}$$

Such a correction would be necessary for any situation in which the freezing point of water is different from T_0. This arises in other instances than in pores, such as in the calculation of equilibrium pressures for bulk hydrate formation involving a gas whose solubility has an effect on the freezing point of water (and therefore T_{Q1}).

Given a specific temperature, T_f, and pore radius, r, the following procedure was followed to obtain P_f. First, for the given radius, the quadruple point temperature was found by solving eq 7 for the $P-T$ curves in both the liquid- and solid-water regions and determining their intersection. Because of the dependence of the second term of eq 7 on T_{Q1}, this was done by an iterative procedure. Equation 8 was used as an initial guess for T_{Q1}. Equation 8 may not give the correct quadruple point temperature, due to the effects of solubility and other considerations which are incorporated in eq 7 that can have an effect on the quadruple point. As a result, eq 7 was used to find the intersection of the proposed $P-T$ curves and thereby obtain an improved estimate of the quadruple point. This process was repeated until T_{Q1} was obtained to the desired accuracy. Once the quadruple point temperature was known, the formation pressure (P_f) was obtained from eq 7 for each formation temperature (T_f) of interest by applying the secant method, augmented by bisection in the advent that the former method failed.[13] The Soave–Redlich–Kwong equation of state[2] was used to calculate the fugacity of the gas and along with the gas solubility can be used to calculate the mole fraction of water in the water-rich phase[2] (note that for methane and propane solubility can be ignored[9]):

$$X_w = 1 - X_g = 1 - \frac{f}{h_w \exp\left(\frac{P\bar{V}}{RT}\right)} \tag{10}$$

where the Henry's law constant h_w is given by[2]

$$\ln(h_w) = -\left(h_w^{(0)}/R + h_w^{(1)}/RT + h_w^{(2)} \ln(T)/R + h_w^{(3)} T/R\right) \tag{11}$$

with the parameter values being taken from Table 5.3 of the literature.[2]

Henry et al.[4] and Clarke et al.[5] reported calculations based on equations similar to eq 7 for comparison with the experimental data of Handa and Stupin[3] for methane hydrate formation in silica gel pores having a nominal radius of 7 nm. [We note that no mention is made in these works[4,5] of the modification that is necessary due to the change in quadruple point temperature in this restricted geometry.] In both of these works,[4,5] the quality of the fits of the model to experimental data is of much lower quality than those obtained for calculations in the bulk. In particular, a large error is observed in the slope of the $P-T$ equilibrium curve. Clarke et al.[5] also present calculations for the formation of propane hydrate in the same size pores, with even less satisfactory results

(13) Cheney, W.; Kincaid, D. *Numerical Mathematics and Computing,* 3rd ed.; Brooks/Cole Pub. Co.: Pacific Grove, CA, 1994; pp 82–119.

Table 1. Parameter Values for Bulk Hydrate Formation

property	unit	bulk value for methane	bulk value for propane
$\Delta\mu_w^0$	J/mol	1263[2]	883.8[2]
$(\Delta H_w^0)_{ice}$	J/mol	1389[2]	1025[2]
$(\Delta H_w^0)_{liq}$	J/mol	−4622[2]	−4986[2]
	ΔC_p^0 J/(mol K)	−34.583[11] $T > T_0$ 3.315[11] $T < T_0$	−38.8607[11] $T > T_0$ 1.029[11] $T < T_0$
ΔV_w	m³/mol	2.9959×10^{-6} [b]	3.39644×10^{-6} [b]
σ_{hw}	J/m²	0.0267[4]	0.0267[4]
b	J/(mol K²)	0.189[11] $T > T_0$ 0.121[11] $T < T_0$	0.18090[11] $T > T_0$ 0.00377[11] $T < T_0$
A_j	K/atm	0.0007372[a] (small cavity) 0.025354[a] (large cavity)	0.0[a] (small cavity) 0.0017634[a] (large cavity)
B_j	K	3267.99[a] (small cavity) 2782.94[a] (large cavity)	0.0[a] (small cavity) 4945.94[a] (large cavity)

[a] These values were obtained by fitting eq 5 to the data for bulk methane and propane hydrate formation found in Sloan.[2] [b] Add 1.6×10^{-6} m³/mol in the liquid water region to account for the difference in molar volume between liquid water and ice.

Table 2. Effective Radii Needed To Fit Experimentally Measured[3] Equilibrium Pressures for Propane Hydrate Formation in Nominal 7 nm Silica Gel Pores[a]

T (K)	P_{exp} (MPa)	P_{calc} (MPa)	r_{eff} (nm)	T_{Q1} (K)
253.0	0.079	0.079	2.22	251.8
261.2	0.141	0.141	3.18	258.6
261.2	0.147	0.147	3.23	258.9
262.2	0.151	0.151	3.44	259.8
262.6	0.156	0.156	3.51	260.1
263.2	0.162	0.162	3.66	260.6
263.6	0.165	0.165	3.77	261.0
264.2	0.172	0.172	3.94	261.6
264.6	0.178	0.178	4.04	261.9
265.2	0.187	0.187	4.21	262.3
265.6	0.195	0.195	4.31	262.6
266.0	0.203	0.203	4.43	262.9
266.6	0.213	0.213	4.63	263.4
267.2	0.224	0.224	4.87	263.9
267.6	0.234	0.234	5.00	264.1
268.2	0.247	0.247	5.25	264.5
268.8	0.264	0.264	5.49	264.9
269.6	0.284	0.284	5.91	265.5
270.0	0.300	0.300	6.04	265.7
270.8	0.319	0.319	6.63	266.4
270.8	0.325	0.325	6.52	266.3
271.2	0.338	0.338	6.81	266.6
271.8	0.357	0.357	7.30	267.0
272.0	0.370	0.370	7.35	267.1

[a] Also shown are the fitted pressures and quadruple point temperatures for the specified effective radii and temperatures.

(deviations of up to 29% were reported between the predicted and experimental equilibrium pressures) than they obtained for methane hydrate. Figure 1 shows the results of using eq 7 along with the parameter values given in Table 1 to calculate equilibrium pressures for methane and propane hydrates. In accordance with the findings of Handa,[14] we have used the experimentally determined value of 7 nm for r in these calculations. Also shown are the corresponding results for the formation of these hydrates in the bulk. As can be seen, only at the highest and lowest temperatures is the fit for propane hydrate even somewhat adequate. An explanation of these differences is needed. As Handa et al.[14] reported, silica gel of 7 nm nominal pore radius actually contains a broad distribution of pore sizes, and according to eq 8, every pore has a different quadruple point temperature. Thus,

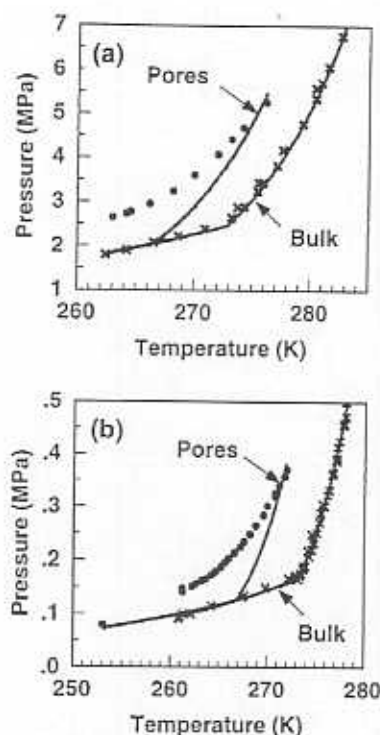(14) Handa, Y. P.; Zakrzewski, M.; Fairbridge, C. *J. Phys. Chem.* 1992, 96, 8594.

Figure 1. Equilibrium pressures for (a) methane and (b) propane hydrate formation in 7 nm (nominal radius) pores (●) and in the bulk (×) are shown as functions of temperature for experimental data as well as model simulations (solid traces).

every pore size confers an additional degree of thermodynamic freedom, so that eq 7 with a single value of r cannot possibly describe the real system. Although it may appear from the way the experiment is conducted that P is a function of T only, the phase rule tells us that the true equilibrium is described by a surface P that is a function of T and r. The key to interpreting pressure–temperature data for real porous media is the recognition that eq 7 can be used to interpret such data if the values of all of the parameters in the equations other than r are known. Then, as explained in the next section, the r for each experimental (P, T) point can be calculated. In fact, the values of all of the parameters in (7) outside of the capillary pressure term are known if measurements have been made on the bulk hydrate and described by the original van der Waals–Plateeuw equation. Then, only the value of $\cos(\theta)\sigma$ is needed to compute the $P(T,r)$ surface and to determine where the experimentally observed data lie on the surface.

The three groups of authors who have addressed calculations for hydrate equilibrium in porous media (Clarke et al.,[5] Uchida et al.,[7] and Henry et al.[4]) have proposed two different interfaces as the source of the capillary pressure term and thus two different values of $\cos(\theta)\sigma$. It is difficult to propose any direct, "visual" observation within the pores to examine which interface is the appropriate one. However, as shown in the next section, by the method described here it is possible to calculate the pore size distribution for any proposed value of $\cos(\theta)\sigma$ and compare the pore size distribution as calculated from that value and the hydrate data with the pore size distribution calculated from conventional nitrogen desorption measurements. Excellent agreement (Figure 6) has been obtained in this way, allowing us to deduce the correct value for the interfacial tension and to infer the identity of the two phases that participate in the interface.
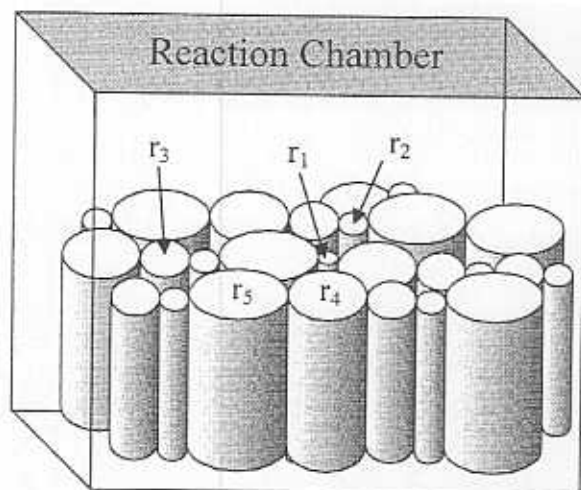

Figure 2. Hypothetical porous medium for use in the conceptual model. Shown are representations of several of the tube sizes which could make up the medium.

Results and Discussion

Clarke et al.[5] propose that the deviations between the calculated and measured equilibrium pressures for the 7.5 nm silica gel pores may be due to the distribution of pore sizes present in the sample. This explanation is motivated by the earlier observation of Handa and Stupin[3] that the gradual change in the slope of the $P–T$ envelope is mainly due to a distribution of pore sizes, leading to the absence of a well-defined, unique quadruple point. The model represented by eq 7 does not consider such a distribution of pore sizes and shows the more commonly observed distinct change in slope at the unique quadruple point. In fact, consideration of the effect of a pore size distribution can account for the deviation of the measured pore equilibrium pressures from those for the bulk in what has been supposed to be the "ice region" in the porous media. To understand this possibility, we make reference to the simplified conceptual model for porous media commonly referred to as the "bundle of tubes" model.[15] Consider the simplified picture of a porous medium shown in Figure 2. We will consider the medium to be made up of tubes of radii $r_1 < r_2 < r_3 < r_4 < r_5 \ldots$, where the spaces between tubes are assumed to be solid substrate. If we had a series of samples each made up of exclusively one size tube, then the equilibrium pressures necessary to stabilize the hydrate in the various samples would be given by $P_1, P_2, P_3, P_4, P_5 \ldots$, with $P_1 > P_2 > P_3 > P_4 > P_5 \ldots$. A more realistic representation of porous media includes a distribution of these tubes such that in a given sample there are N_i tubes of radius r_i. Additionally, we consider the total volume of gas that could be present in such tubes as guest molecules in hydrates (if all appropriate cavities were occupied) to be equal to V_i^g. Now consider a sample of a porous medium with various size tubes where the tubes are filled with hydrate and the reaction chamber is kept under conditions such that the hydrate is stable for all of the tube sizes present. As the temperature is raised, the point will eventually be reached where the gas pressure in the chamber is not sufficient for all of the hydrate to remain stable, and some of it will start to decompose. Since smaller radius tubes require larger pressures for the hydrate to remain stable, the smallest tubes will be the first to decompose. As shown in Figure 2, there is a certain amount of free space exterior to the porous medium

(15) Fatt, I.; Dykstra, H. *Trans. AIME* **1951**, *192*, 249.

and interior to the reaction chamber that we will call the headspace. As the hydrate in the smallest tubes decomposes, gas is given off, raising the pressure in the headspace. If the volume V_1^g (the total volume of gas available from tubes of radius r_1) is more than sufficient to raise the pressure up to P_1 (the pressure necessary to stabilize the hydrate in tubes of radius r_1 at the current temperature), then equilibrium will be reestablished before all of the tubes of radius r_1 are exhausted, and the experimentally observed pressure at this temperature will be that which would be observed if the medium were solely made up of tubes having this radius. If, due to the volume of the headspace, these tubes do not contain a large enough volume of gas to raise the pressure by the required amount, then all of the hydrate in tubes of this size will decompose, and that in the next size tubes (having radii r_2) will begin to decompose. If the total volume from these two tube sizes ($V_1^g + V_2^g$) is more than sufficient to raise the pressure up to P_2, then not all of the hydrate in this size tube will decompose, and the experimentally observed pressure at this temperature will be that which would be observed if the medium were solely made up of tubes having radius r_2. Therefore, with this conceptual model for hydrate decomposition in porous media, at each temperature the measured equilibrium pressure corresponds to that for a single size tube, but the size of the tube will vary as the temperature is varied. This implies that the relevant r value in eq 7 varies as one moves along the experimental $P-T$ curve for silica gel shown in Figure 1. A reciprocal argument can be made about the formation of hydrate in porous media, where it would be the largest tubes that would fill with hydrate first, since they require the lowest pressures for the hydrate to be stable.

Since eq 7 only yields results different from those for the bulk when the equilibrium involves liquid water, any deviation in the observed equilibrium pressure from that for the bulk indicates the presence of liquid water (not ice) in the pores involved in the equilibria. As shown by eq 8, the water in each size pore has a different freezing point. As a result, some (smaller) pores will contain liquid water at the same time that other (larger) pores contain ice. Since the initial equilibrium measurements (which are at the lowest temperatures) involve the smallest pores, the observed equilibrium would only involve ice if one started at temperatures below the freezing point of water in the smallest pores originally filled with hydrate. Examination of Figure 1b shows the one datum point reported by Handa and Stupin at 253 K for propane hydrate that appears to be just above the freezing point of the water contained in the pores involved in the equilibrium. This is inferred from the small deviation of the observed equilibrium pressure from that expected for bulk hydrate decomposition involving ice and free gas. All of the other data points in Figure 1 appear to be at sufficiently high temperatures to result in the equilibria involving liquid water. Had the experiments been initiated at a lower temperature, we believe more data points would have corresponded to equilibria involving ice rather than liquid water.

If the above conceptual model is correct, we should be able to determine a different r value for each datum point on the $P-T$ curve, which allows eq 7 to reproduce the experimentally observed equilibrium pressures. In addition, these radii must be such that the quadruple points in the pores involved in the equilibria are below the temperatures in the reaction cell, meaning that the equilibria are between liquid water and hydrate, not ice and hydrate. To explain the deviation of the observed

pressures from those for the bulk, this must be true for all of the experimental data points, since pore size only has an effect on the hydrate–liquid water equilibrium. As a first test of this model, we seek values of r that allow eq 7 to reproduce each of the experimental data points individually and then examine which phase the water will be in for such pores at the experimental temperatures. If we can find such values of r and if the temperatures are such that the water would be in the liquid state, then the model will have demonstrated that the data are explainable by the model, and we shall have determined the effective pore size for each data point. Once this is done, the complete pore volume distribution can be reconstructed and compared with data from nitrogen desorption isotherms.

The above equations are used in the following manner. At each temperature the procedure described above is used to calculate the equilibrium pressure, and the error between the observed and calculated equilibrium pressure is minimized using Brent's method[16] with the value of r as an adjustable parameter. Obviously, each change in r necessitates the determination of a new quadruple point temperature, as discussed below eq 9. Note that the pressures reported here have been corrected for the vapor pressure of water.

The comparison of the experimental equilibrium pressures reported by Handa and Stupin[3] and the best fits found using eq 7 are shown in Table 2 for propane hydrate. As can be seen, the calculated equilibrium pressures have been exactly matched to the experimental ones through an appropriate choice of pore radius at each temperature. The r values used to obtain this fit, and the corresponding quadruple point temperatures are also given in Table 2. In examining the r values, we note that for the lowest experimental temperature (253 K) the fit requires a radius of approximately 2.22 nm. Since T_{Q1} for this pore size is 251.8 K (see Table 2), the water in a 2.22 nm pore would be liquid at 253 K, explaining why the equilibrium pressure is different from (but very close to) that for dissociation of hydrate to ice and free gas at that temperature. For all of the experimental points and values of r in Table 2, T_{Q1} is less than T_f. Similar calculations done for the methane hydrate data presented by Handa and Stupin[3] also result in exact fits and have the same general behavior as that described for propane. This establishes the self-consistency of our conceptual model, since it shows that the predicted radii put all of the data in the liquid water region, and the model thus passes its first test.

Seshadri et al.[6] repeated the measurements of Handa and Stupin[3] for propane hydrate in silica gel of nominal pore size 7.5 nm and extended the technique to silica gels of nominal pore radii 2, 3, and 5 nm. Figure 4 in the literature[6] shows the experimentally observed equilibrium pressures in pores with nominal radii of 2, 3, 5, and 7.5 nm for propane hydrate reported by Seshadri et al.[6] Fitting of eq 7 to these data results in exact fits, as in the above cases. The values of the pore radii for each set of data and at each of the experimental temperatures are depicted in Figure 3, along with those used for the data of Handa and Stupin[3] for propane. Since the equilibrium pressure is actually a function of both pore size and temperature, Figure 3 is the projection of a collection of points on this surface onto the $T-r$ plane, while Figure 1 in this work and Figure 4 in the literature[6] are projections onto the $T-P$ plane. The full surface has been calculated using eq 7, and is shown in Figure 4, where the data depicted in

(16) Brent, R. P. *Algorithms for Minimization Without Derivatives*; Prentice Hall: Englewood Cliffs, NJ, 1973; Chapter 7.
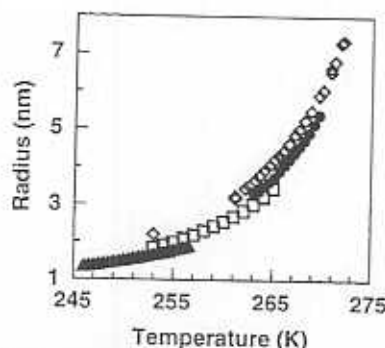
Figure 3. Radii needed to fit eq 7 to experimentally measured equilibrium pressures for propane hydrate formation in silica gels of nominal pore radii 2 (▲), 3 (□), 5 (●), and 7.5 (◇) nm as a function of temperature.
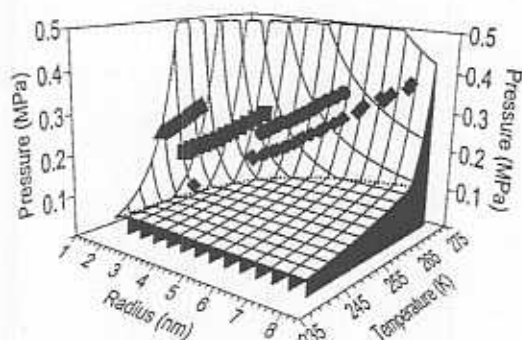

Figure 4. Calculated equilibrium pressure as a function of temperature and pore radius for propane hydrate formation. The quadruple point temperature−pressure curve is indicated by the dotted trace. Also shown are the experimentally measured equilibrium pressures in silica gels of nominal pore radii 2 (▲), 3 (■), 5 (●), and 7.5 (◆) nm.

Figures 1 and 3 of this work, and Figure 4 of the literature[6] have been superimposed. Also shown in Figure 4 is a dotted curve representing the quadruple point temperature and pressure as a function of pore radius. The quadruple point temperature and pressure are plotted as functions of $1/r$ in Figure 5 so that the values for the model can be compared with the bulk values for large r ($1/r \rightarrow 0$).

As a further test of the conceptual model presented here, the calculated pore radii and the observed equilibrium temperatures and pressures are used to calculate the pore volume distribution for the silica gel with the largest nominal pore size, and this distribution is compared with that obtained from nitrogen desorption isotherms.[17] To determine the distribution, the molar volume of the gas, v_i, is calculated by means of its equation of state for each experimental temperature and pressure (T_i, P_i). The change in the number of moles of gas in the system in going from state i to state $i + 1$ is then given by

$$\Delta n_{i,i+1} = V_{sys}\left(\frac{1}{v_{i+1}} - \frac{1}{v_i}\right) \tag{12}$$

where V_{sys} is the volume of the headspace. Given that the number of gas molecules contained in a unit cell of hydrate is n_{cell} and that the volume of each unit cell is V_{cell}, the total volume of the pores from which the hydrate decomposed to cause the pressure increase from P_i to P_{i+1} per gram of silica gel is given by

(17) Lowell, S.; Shields, J. E. *Powder Surface Area and Porosity;* Chapman and Hall: New York, 1991; pp 52–71.
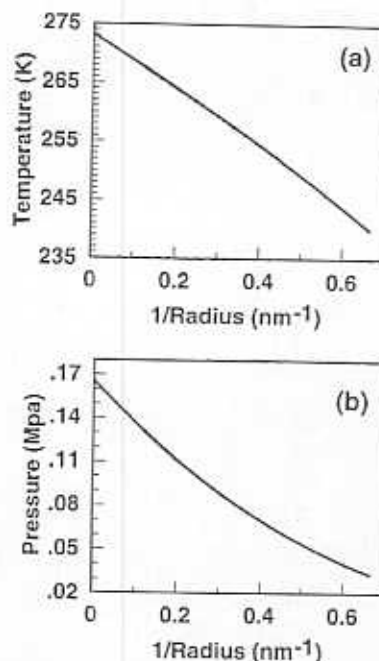
Figure 5. Quadruple point temperature (a) and pressure (b) for propane hydrate as functions of the reciprocal of pore radius. The quadruple point temperature and pressure for the bulk occur at $1/r \rightarrow 0$ nm^{-1} and are 273.15 K and 0.165 MPa, respectively.

$$\Delta V_{i,i+1} = \frac{V_{cell} N_A}{n_{cell} W_{gell}} \Delta n_{i,i+1}$$

$$= \frac{V_{cell} V_{sys} N_A}{n_{cell} W_{gell}}\left(\frac{1}{v_{i+1}} - \frac{1}{v_i}\right) \tag{13}$$

where w_{gell} is the weight of silica gel used in the experiment and N_A is Avogadro's number. While V_{cell} is known and n_{cell} can be estimated on the basis of the fractional occupancy of the cages, V_{sys} and w_{gell} are not known for some of the results in the literature. In addition, this only gives an estimate of the volume of water involved in the formation of hydrate and would not include the volume occupied by water not involved in this process (which may be significant for small pores). To compensate for these difficulties, the results are normalized so that the largest $\Delta V_{i,i+1}$ has a magnitude of unity. Since the results obtained from the desorption isotherms also are on a per gram of silica gel basis, the same is done for the volume change as a function of pore radius obtained from these data. The distribution resulting from applying this approach to the data in the literature is shown in Figure 6. Figure 6a shows the results of using the propane hydrate data of Seshadri et al.[6] (triangles) as well as the distribution obtained from desorption measurements done on the same silica gel as that used in the experiments[6] (solid trace). The agreement between the two distributions seems to be very good, supporting the validity of the model. The corresponding plot using the results of Handa and Stupin[3] is shown in Figure 6b, where both the methane and propane data have been used. Note the slight shift of the calculated distribution away from that obtained from desorption measurements on the silica gel used by Seshadri et al.[6] This may be due to a small difference in the silica gel samples used in these two sets of experiments. As noted by Handa and Stupin,[3] they determined the mean
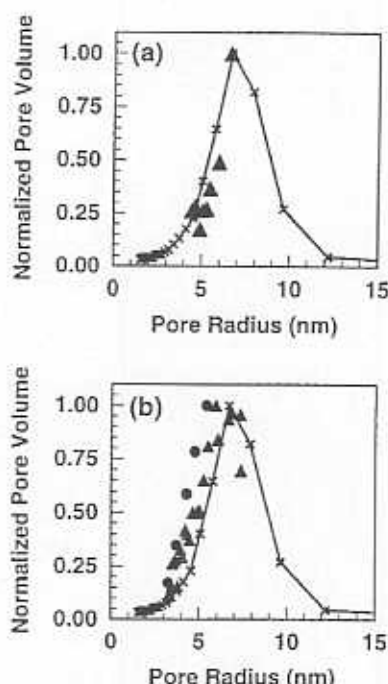
Figure 6. Normalized pore volumes reconstructed from propane (▲) and methane (●) hydrate data for silica gel pores based on the data of (a) Seshadri et al. and (b) Handa and Stupin. Also shown are results based on nitrogen desorption isotherms (solid traces).

pore size of their sample to be 7.0 nm, which is different from the 7.5 nm value reported by the manufacturer and found by Seshadri et al. The fact that Figure 6b is based on two separate reconstructions, one for a structure I hydrate (methane) and the other for a structure II hydrate (propane), and that the reconstructed distributions correlate so well with each other as well as the experimentally determined distribution seems to further validate the proposed conceptual model.

In the treatments of Henry et al.,[4] Uchida et al.,[7] and this paper, the hydrate–liquid water is the operative interface. Apparently the tension of this interface has not been reported; both Uchida et al.[7] and Henry et al.[4] suggested that it could be approximated by the tension for the ice–liquid water interface. Uchida et al.[7] suggested the value 0.039 J/m^2; Penner[18] estimated it to be between 0.003 and 0.0035 J/m^2; Fletcher[19] places the value between 0.001 and 0.003 J/m^2; Henry et al. used the value 0.0267 J/m^2, which is also the value used here (Table 1). Figure 6 illustrates the excellent agreement obtained for the pore volume distribution as obtained from (1) nitrogen absorption/desorption measurements, (2) the tension 0.0267 J/m^2 and data for an sI hydrate, and (3) the tension 0.0267 J/m^2 and data for an sII hydrate. In addition to testing the model, this agreement also suggests that the sI–liquid water tension, the sII–liquid water tension, and the ice–liquid water tension may indeed be equal within the sensitivity required for present purposes.

The model used here allows a further test of this tension hypothesis. According to the model, when the experimental temperature is below the quadruple point of the smallest pore within which hydrate formed (so that for all pores the equilibrium is between hydrate and ice with free gas),

the equilibrium pressure above the sample should be the same as for the bulk hydrate (because the hydrate–ice tension is approximately zero). The lowest temperature measurement of Handa and Stupin[3] (Figure 1b) provides a single-datum test of this prediction of the model and the 0.0267 estimate for the sII hydrate–liquid water tension. This experimental point does, indeed, fall very close to the equilibrium line extrapolated from higher-temperature measurements[2] for the bulk propane hydrate. Unpublished measurements by others in our group on ethane hydrate in porous media show a similar agreement with bulk-hydrate pressures. Thus, while a direct (e.g., sessile drop) measurement of the sI–liquid water and sII–liquid water tensions is desirable, measurements on hydrates in porous media may themselves provide experimental estimates for these interfacial tensions.

Conclusions

For hydrate formation in silica gel pores, an explanation has been proposed for the discrepancy between experimental data[3,6] and previous calculations.[4,5] This explanation is able to reproduce the experimentally observed equilibrium pressures as a function of temperature in pores of nominal radii 2, 3, 5, and 7.5 nm as well as the apparently smooth changes in the slopes of the experimentally observed P–T equilibrium curves for the porous media. Unlike previous models,[4,5] which assume that only a single pore size is present, the revised model for the dissociation of hydrate in porous media considers the pore size distribution. The revised model also explains the differences between experimentally observed equilibrium pressures for bulk hydrate and for hydrates in pores at the temperatures where the latter equilibrium was assumed to be among gas, ice, and hydrate, where surface tension effects should have no influence on the equilibrium pressure in the pores. The presented interpretation predicts that the apparent smooth change of the slope in the pressure–temperature curves is due to a change in the effective radius of the pores involved in the equilibrium as one moves along the P–T equilibrium curve. The proposed model predicts that the equilibrium always involved liquid water at the temperatures that so far have been studied experimentally.[3,6] The model predictions were also used to reconstruct pore volume distributions. The results of this analysis were in good agreement with the distribution obtained from desorption isotherms for the nominal 7.5 nm pores.

The proposed conceptual model suggests that the equilibrium pressures observed in pores are dependent on both the headspace and the amount of sample present, since both of these will affect which size pores are involved in the equilibrium at a specified temperature. In addition, it leads to the conclusion that the equilibrium is between hydrate and liquid water for all of the experimental data considered here. Further studies need to be performed to further test this model. For example, a set of experiments in which the sample size-to-headspace ratio was varied might show whether indeed these quantities have an effect on the observed equilibrium pressure. Other experiments, such as NMR, designed to determine the state of the water in equilibrium with the hydrate would help to further test the validity of this model.

(18) Penner, E. Physics of Snow and Ice. *Proc. Int. Conf. Low-Temp. Sci.* 1996, 1401.

(19) Fletcher, N. H. In *The Chemical Physics of Ice*; Cambridge University Press: Cambridge, 1970; p 96.